



Selective transformation of methyl and ethyl mercaptans mixture to hydrocarbons and H₂S on solid acid catalysts



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ABSTRACT

The catalytic conversion of C₂H₅SH on protonic molecular sieves, i.e. ZSM-5 with various Si/Al ratios, Ferrierite, Y, SAPO-34, was studied in a gas flow reactor. Ethylene and H₂S are the main products, but small amounts of C1–C4 alkanes, C6–C8 aromatics, coke, CS₂ and thiophenes are formed. The catalytic behavior strongly depended on both acidic and textural properties of solids. Assuming a pseudo first order kinetic model, the rate constant and the activation energy have been evaluated for all catalysts. Over the best catalytic material, H-ZSM-5 (Si/Al = 15), full conversion of C₂H₅SH was achieved at temperature higher than 673 K. Additionally, the catalyst lifetime measured at 823 K was more than 70 h of time-on-stream. With C₂H₅SH/CH₃SH mixture, over H-ZSM-5, the conversion of thiols was total at 823 K for at least 11 h. In that case, significant amounts of coke and aromatics were formed, but after the thermal regeneration with air, the spent catalyst recovered the properties of the fresh zeolite.

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1. Introduction

Sulfur is invariably an abundant heteroatom impurity in fossil sources such as natural gas, crude oil and coal. In the natural gas, sulfur is mainly present in the form of hydrogen sulfide (H₂S), carbonyl sulfide (COS) and C1–C3 mercaptans (thiols). After a deacidification process with conventional amine solvent, the gas still contains up to 30 ppmv total sulfur, mainly as mercaptans and COS. For environmental and industrial reasons, their concentration in natural gas needs to be kept below 5 ppmv. Modern processes for deep removal of COS are based on fixed bed adsorption and catalytic hydrolysis [1,2]. Commercial processes used to remove the mercaptans from gas usually request formulated solvent or include reactions calling for additional reagents (O₂, H₂, olefins, NaOH, etc.), which often generate wastes. We have recently shown that the methyl mercaptan can be selectively transformed into hydrocarbons and H₂S at high temperatures in the presence of protonic zeolites, without requiring the addition of any reagent [3,4]. The produced H₂S can be efficiently eliminated by conventional deacidification processes with amine solvents associated to Claus process.

C₂H₅SH is together with CH₃SH a common mercaptan present in the natural gas. For that reason, in continuation of our research efforts in the field of gas desulfurization [2–4], this work is dedicated to analyze and optimize the catalytic conversion of C₂H₅SH over different protonic zeolites, including ZSM-5 with various Si/Al ratios, ferrierite, Y and SAPO-34. The catalytic conversion of mixtures C₂H₅SH and CH₃SH has also been investigated. It should be noted that the decomposition of C₂H₅SH in an inert gas flow has been previously studied on solid catalysts such as alkali metal zeolites [5–7], alkaline earth and transition metals zeolites [8,9], Al₂O₃ [8], MgO and CaO [8,9], NiS and CdS [10]. Tests performed at temperature in the range 573–723 K have shown that the main products were ethylene, alkanes, aromatics, thiophene, diethylsulfide and coke [5–10]. However, only few data relating to the catalytic conversion of ethylmercaptan over zeolites in hydrogen form can be found in open literature [7–9,11,12]. The reaction has been achieved at 623 K and 673 K, in the presence of H-Y, H-X or H-ZSM-5 zeolites, and the products were ethylene, diethyl sulfide and H₂S [9,11,12]. Besides zeolites with MFI and FAU topology, in this study we explored for the first time the behavior of other microporous materials, i.e. ferrierite (FER) and SAPO-34 (CHA). The catalytic tests were performed on a larger temperature range, from 623 to 823 K. Furthermore, we evaluated the kinetic parameters for the C₂H₅SH decomposition over various zeolites and we studied the simultaneous decomposition of C₂H₅SH and CH₃SH.

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Table 1

Some characteristics of the catalysts.

Catalysts	Si/Al	Main pore size ^a (Å)	Surface _{BET} (m ² g ⁻¹)	Micropore volume (mL g ⁻¹)	Acid sites ^b (mmol g ⁻¹)	Bronsted sites ^c (mmol g ⁻¹)
H-ferrierite	10	5.4 × 4.2	268	0.111	1.82	0.84 [14]
H-SAPO-34	–	3.8 × 3.8	549	0.250	1.03	–
H-Y	15	7.4 × 7.4	696	0.232	0.89	0.46 [15]
H-ZSM-5(15)	15	5.1 × 5.5	378	0.119	1.31	0.69 [15]
H-ZSM-5(40)	40	5.1 × 5.5	443	0.130	0.44	–
H-ZSM5-5(75)	75	5.1 × 5.5	388	0.061	0.20	–

^a From Atlas of zeolite structures (<http://www.iza-structure.org/default.htm>).^b The number of acid sites was determined from the amount of NH₃ desorbed in TPD experiments.^c Measured via pyridine FTIR.

2. Experimental

2.1. Catalysts and chemicals

Commercial zeolites NH₄-ZSM-5 (CBV 3024E – Si/Al = 15, CBV 8014 – Si/Al = 40), H-Y (CBV 720; dealuminated Y faujasite with Si/Al ratio of 15), NH₄-FER (CP914C – Si/Al = 10) were provided by Zeolyst International. H-SAPO-34 and H-ZSM-5 (Si/Al = 75) were obtained from TOTAL SA. Before the catalytic tests, the materials were calcined in air during 6 h at 823 K to obtain their active hydrogen form. Gas cylinders of dinitrogen, C₂H₅SH/N₂ (0.25/99.75, v/v), C₂H₅SH/N₂ (5.0/95.0, v/v) and CH₃SH/N₂ (5.0/95.0, v/v), purity of all >99.995% (v) were supplied by Air Liquide.

2.2. Characterization

The porous structure of the catalyst was evaluated by N₂ sorption. The experiments were conducted at 77 K using a Micromeritics ASAP 2010 sorptometer. The samples were desorbed under vacuum at 573 K for 15 h. N₂ isotherm is used to determine the apparent surface area with BET approach and the micropore volume.

The number of acid sites was evaluated by temperature programmed desorption (TPD) of ammonia using a Micromeritics AUTOCHEM 2910 apparatus. The sample (around 0.1 g) was first heated at 823 K in air flow for 6 h. Then it was saturated with NH₃ by flowing a 5% (v) NH₃/He mixture at 373 K during 30 min. After that, the sample was purged for 2 h in a He flow to eliminate loosely bonded NH₃. Finally it was heated at a constant temperature ramp-up of 10 K min⁻¹ up to 873 K in He flow (30 ml min⁻¹). The NH₃ concentration evolving from the sample during the last heating step was continuously measured by a thermal conductivity detector (TCD).

For the quantification of the coke deposit in the catalyst, the microreactor was flushed with nitrogen at 823 K at the end of the reaction, in order to desorb any adsorbed species on the surface of the catalyst. 20 mg of the used catalyst was then analyzed by thermogravimetry (TGA) with a NETZSCH TG 209C apparatus. The temperature program started with an isothermal period of 5 min at 298 K and then a temperature ramp up to 1173 K at 10 K min⁻¹ in synthetic air took place. The weight loss between 723 and 1023 K was attributed to the burning of coke.

The main characteristics of the catalysts are given in Table 1.

2.3. Catalytic activity measurements

The catalytic conversion of mercaptans in various feed compositions was carried out in a stainless steel fixed-bed microreactor (4 mm i.d.) at atmospheric pressure. The composition of the reactor feed was adjusted with flow meters, in order to obtain the following gas mixtures: C₂H₅SH/N₂ (0.25/99.75, v/v), CH₃SH/C₂H₅SH/N₂ (0.5/0.225/99.275, v/v/v) and CH₃SH/C₂H₅SH/N₂ (0.2/0.4/99.4, v/v/v). In order to minimize the influence of the external mass transfer and intra-particle diffusional resistances on the rate

process, conventional procedures (varying the gas feed/catalyst weight ratio and the particle size) were performed before the catalytic study. Standard experiments were performed with a 100 mg bed of catalyst (grain size of 150–250 μm) supported by glass wool, at weight hourly space velocities (WHSV) of mass_{C₂H₅SH}/mass_{catalyst} 0.32 h⁻¹ and mass_{CH₃SH}+mass_{C₂H₅SH}/mass_{catalyst} of 0.32 or 0.50 h⁻¹. In some experiments, the gas feed was previously saturated with water. The products were analyzed online by gas chromatography, using a dual detector device (flame ionization detector and flame photometric detector) and a dual column device (Supel-Q Plot and DB-17 Agilent J&W) [3].

2.4. Kinetic study

A kinetic study was carried out in order to evaluate the rate constants and the activation energies. For this purpose a pseudo first order reaction rate is assumed for C₂H₅SH decomposition, as suggested by Sugioka and Aomura [9,13]. The reaction rate is expressed as: $r = k \times C_{C_2H_5SH}$; where k is the kinetic constant (cm³ s⁻¹ g_{cat}⁻¹) and $C_{C_2H_5SH}$ represents the C₂H₅SH concentration (mol cm⁻³). Assuming that the reactor is a constant pressure plug flow type, the relationship between the contact time (τ , s g_{cat} cm⁻³) and the conversion is expressed by the following equation:

$$\tau = \frac{m_{cat}}{Q_{in}} = C_{C_2H_5SH}^{in} \int_0^{x_f} \frac{dx}{r(x)} \quad (1)$$

where Q_{in} is the flow rate, in cm³ s⁻¹ and x_f is the final conversion.

For a first order reaction, Eq. (1) can be written in the following form:

$$k\tau = -\ln(1 - x_f) \quad (2)$$

The evaluation of the final conversion (x_f) at a given temperature and a fixed residence time (τ) allows calculating the kinetic constant, k .

Using the Arrhenius law, finally we can write:

$$\ln k = \ln \left[\left(-\frac{1}{\tau} \right) \ln(1 - x) \right] = \ln k_0 - \frac{E_a}{RT} \quad (3)$$

For all catalysts, we first verified that the reaction rate was of the first order. For this purpose, decomposition tests were performed at 613 K varying the residence time (τ). The linear relationship between $\ln(1 - x_f)$ and τ proved the validity of the assumption (Eq. (2)). As a consequence, a single decomposition test at a fixed τ was sufficient to evaluate k at higher temperatures (633–673 K).

A linear regression of plotted $\ln k$ versus $1/T$ allowed calculating the activation energy (E_a) (Eq. (3)).

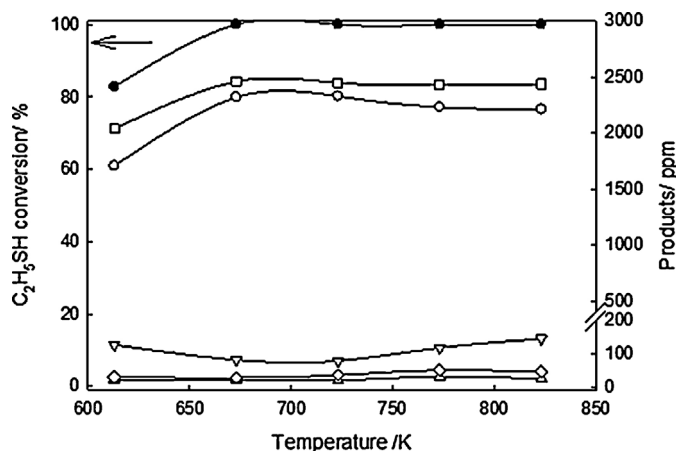


Fig. 1. Conversion of C_2H_5SH vs. temperature on H-ZSM-5(15); (●) conversion; concentrations: (□) H_2S , (○) C_2H_4 , (▽) C1–C4, (◇) thiophene + CS_2 , and (△) BTX.

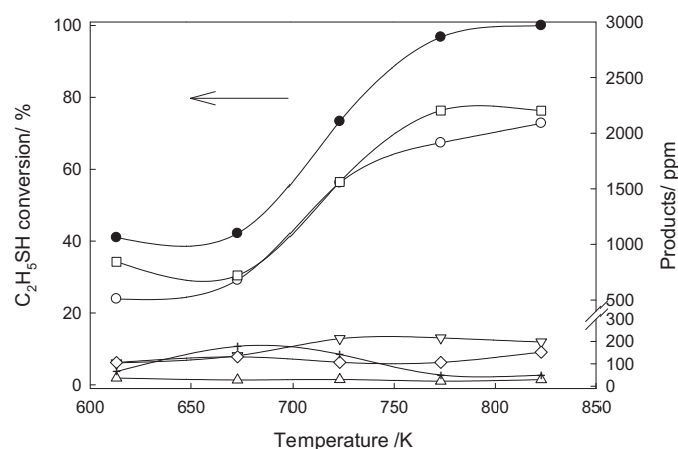


Fig. 2. Conversion of C_2H_5SH vs. temperature on H-SAPO-34; (●) conversion; concentrations: (□) H_2S , (○) C_2H_4 , (▽) C1–C4, (◇) thiophene + CS_2 , (△) BTX, (+) S residual.

3. Results and discussion

3.1. Catalytic conversion of ethyl mercaptan

In a blank experiment carried out without any catalyst (only 1 g of quartz in the reactor) the decomposition of C_2H_5SH started at about 673 K and reached 93% at 823 K (Figure S1, Supplementary information). The formation of ethylene and H_2S largely prevails in this experiment though noticeable amounts of C1–C4 alkanes, as well as CS_2 and thiophene traces are present at 823 K. The catalytic experiments were carried out using the same protonic molecular sieves that have been successfully used for the conversion of CH_3SH to hydrocarbons in our previous studies [3,4]. Thus, H-ZSM-5, H-FER, H-Y and H-SAPO-34 were tested in the temperature range of 623–823 K. For each temperature the catalytic test was carried out using a fresh sample, for 6 h time-on-stream (tos). Fig. 1 shows the results obtained in presence of H-ZSM-5(15). Full conversion is achieved even at 673 K. At that temperature, in absence of a catalyst only 0.6% of C_2H_5SH is converted. With catalyst, ethylene and H_2S are the major products (according to equation $C_2H_5SH \rightarrow C_2H_4 + H_2S$), and only small amounts (50–150 ppm) of C1–C4 alkanes, benzene, toluene and xylene (BTX), CS_2 and thiophene are formed. Traces of diethylsulfide were detected in several tests. Generally, these results are in agreement with those previously reported with protonic zeolites [7–9,11,12].

The profiles of C_2H_5SH conversion as a function of temperature and the products selectivity obtained in the presence of H-SAPO-34 (Fig. 2), H-FER and H-Y catalysts (Figs. S2 and S3, Supplementary information) are analogous to those exhibited by H-ZSM-5(15). However, at lower temperatures, the activity varies with the catalyst and it decreases in the order: H-ZSM-5(15) > H-FER > H-Y > H-SAPO-34. Table 2 summarizes the results obtained at 673 K. Note that for all catalysts the C_2H_5SH conversion and the products selectivity did not significantly change over the 6 h tos. The number of acid sites of these catalysts, evaluated from the TPD of NH_3 is listed in Table 1. Data about the acidity of commercial zeolites are also available in the open literature. For example, the Brønsted acidity of H-ferrierite, H-Y and H-ZSM-5(15) is 0.84, 0.46 and 0.69 $mmol\ g^{-1}$, respectively [14,15]. From the catalytic results summarized in Table 2, it clearly appears that the materials exhibiting the highest concentration of acid sites (H-ZSM-5(15) and H-FER) are the more active too. However, H-FER is less active than H-ZSM-5(15) though containing more acid sites, suggesting that the activity of H-zeolites is controlled not only by the acidity of the zeolite, but also by its topology. As shown in Table 2, the selectivity in the C_2H_5SH transformation also depends on the catalyst topology.

H-SAPO-34 and H-Y produce significant amount of CS_2 + thiophene and C1–C4 alkanes. In contrast, H-ZSM-5 and H-ferrierite produce very large amount of H_2S and ethylene and only traces of other compounds. Over all catalysts, very small amounts of aromatics BTX are obtained. We note that the conversion of CH_3SH over these catalysts led to large amount of BTX hydrocarbons [3,4].

In order to establish a relationship between the number of acid sites and the catalytic activity additional experiments were performed using three zeolites with MFI topology and different Si/Al ratio: H-ZSM-5(15), H-ZSM-5(40) and H-ZSM-5(75). As shown in Table 2 the activity and the selectivity to ethylene follow the order H-ZSM-5(15) > H-ZSM-5(40) > H-ZSM-5(75) according to the number of Brønsted acid sites, which increases decreasing the Si/Al ratio [16]. A similar correlation between the Brønsted acid sites and the conversion of C_2H_5SH over H-Y zeolite has been reported by Sugioka and Aomura [9].

In order to have a deeper insight into the real scale of activities differentiating the catalysts we have carried out a kinetic study between 613 and 673 K. A pseudo first order reaction rate was assumed for C_2H_5SH decomposition (see Section 2). Accordingly, there is a linear relationship between $-\ln(1-x)$ and τ (x : C_2H_5SH conversion, τ : residence time). To prove that, we have carried out different tests at 613 K, by varying the residence time. As shown in Fig. 3a, this model is appropriate for all catalysts. A linear Arrhenius plot of $\ln k$ vs. $1/T$ (Fig. 3b), made between 613 and 673 K, fixing the residence time, led to the activation energy. The kinetic parameters summarized in Table 3 confirm that H-ZSM-5(15) is the more active catalyst. Additionally, a clear correlation exists between the number of acid sites and the kinetic constant for catalysts having the same morphology: k increases with the total acidity, following the order: H-ZSM-5(75) < H-ZSM-5(40) < H-ZSM-5(15).

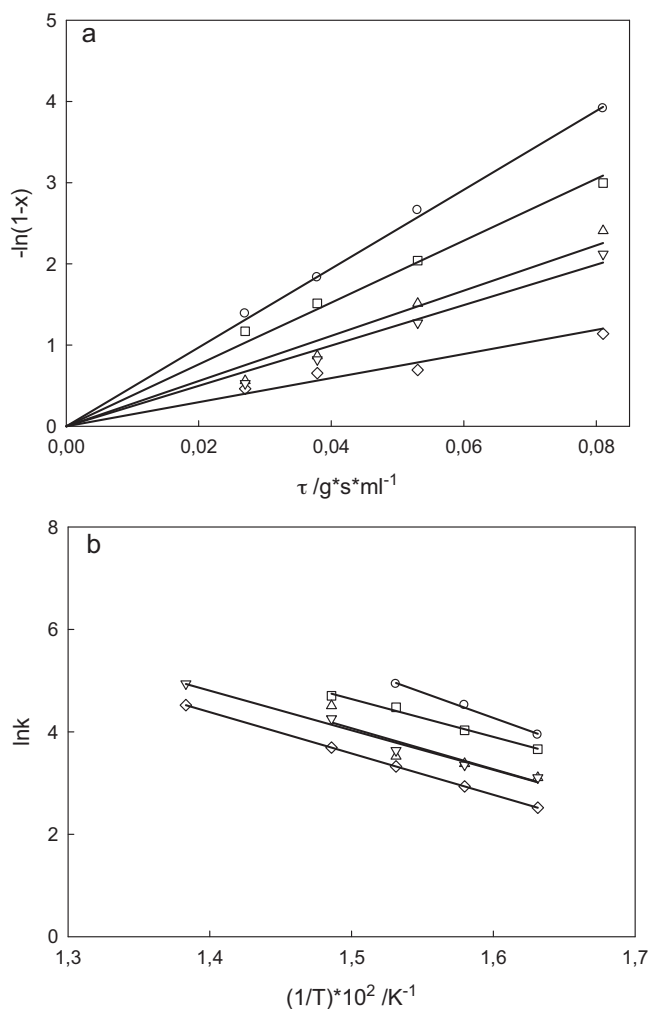
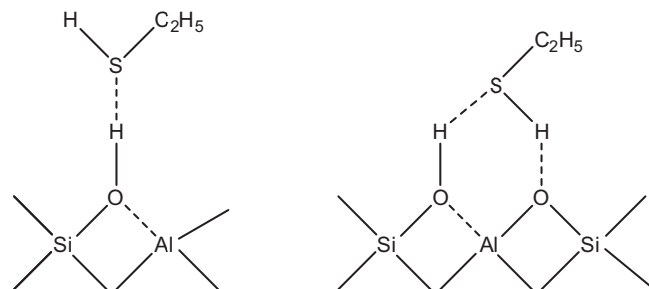
The C-containing products formed in the catalytic C_2H_5SH decomposition were ethylene (as major compound), C1–C4 alkanes, BTX, thiophene and CS_2 . The diethylsulfide was only detected in small amount on H-SAPO-34 and on H-Y. The amount of coke (TGA) was less than 0.5 mg/100 mg for all catalysts. As shown in Table 2 the products distribution significantly depends on the catalyst. Ethylene selectivity reaches 97% on H-ZSM-5(15) and H-FER and is lower with H-Y (90%) and H-SAPO-34 (82%). In this general frame, regarding ethylene selectivity, the catalysts rank according to the number of acid sites: H-FER > H-ZSM-5(15) > H-Y > H-SAPO-34 (Table 2, Figs. 1 and 2, and Figs. S2 and S3 in Supplementary information). In contrast, the selectivities to C1–C4 alkanes, thiophene and CS_2 follow the opposite trend: H-SAPO-34 > H-Y > H-FER > H-ZSM-5(15).

Table 2 C_2H_5SH conversion and product distribution on H-molecular sieves at 673 K and 6 h tos.

Catalyst	C_2H_5SH conv. (%)	Selectivity to S-products ^a (%)		Selectivity to C-products ^a (%)		
		H_2S	Sres ^b	C_2H_4	C1–C4	BTX
H-ferrierite	96.0	98.5	1.5	97.2	2.5	0.3
H-SAPO-34	42.0	87.2	12.8	82.4	16.6	1.0
H-Y	68.5	90.8	9.2	90.1	9.1	0.8
H-ZSM-5(15)	100	99.0	1.0	97.3	2.3	0.4
H-ZSM-5(40)	98	98.4	2.6	96.2	3.5	0.3
H-ZSM-5(75)	92.0	94.0	6.0	91.2	7.7	1.1

^a The selectivity is defined as: (amount of product/amount of total products) \times 100.^b Sres: CS_2 + thiophene.**Table 3**Kinetic parameters for the conversion of C_2H_5SH over zeolites.

Catalyst	Temperature (K)				E_a (kJ mol ⁻¹)
	613	633	653	673	
	k (cm ³ s ⁻¹ g _{cat} ⁻¹)				
H-FER	19.5	29.5	43.5	62.5	66.6
H-Y	12.7	19.2	28.4	40.9	67.0
H-ZSM-5(15)	54.3	90.5	146.2	229.6	82.5
H-ZSM-5(40)	38.8	56.8	81.3	113.4	61.5
H-ZSM-5(75)	19.8	29.5	42.9	61.0	64.5

**Fig. 3.** Kinetic data: (a) $-\ln(1-x)$ vs. τ ; (b) Arrhenius plot. (O) H-ZSM-5(15), (Δ) H-ferrierite, (◇) H-Y, (□) H-ZSM-5(40), and (▽) H-ZSM-5(75)**Fig. 4.** Models for C_2H_5SH adsorbed on H-ZSM-5.

Those results are in line with the literature data. According to previous reports, zeolites in hydrogen form strongly interact with mercaptans like with alcohols [17,18]. Since the mercaptan molecules are more acidic than alcohols, the C–S bond in mercaptans is weaker than the C–O bond in alcohols. Therefore, the C–S bond cleavage is easier than that of the C–O bond [17]. Garcia and Lercher [18] investigated the adsorption of ethyl mercaptan on H-ZSM-5. On the basis of the spectroscopic measurements they found that C_2H_5SH selectively interacts with the Brønsted acid sites (SiOHAl groups) and proposed two probable structures of thiol adsorbed on zeolite (Fig. 4). Such coordinative bonding between sulfur atom and zeolite leads to the weakness of the C–S bond which can be easily broken to form H_2S and $C_2H_5^+$, the latest transformed to ethylene. This mechanism is consistent with the very high selectivity to ethylene and H_2S observed during the ethyl mercaptan conversion on protonic zeolites. Our results are also consistent with those reported by Ziolk et al. [11], who proposed that a stronger Brønsted type acidity favors the formation of ethylene, in contrast with a lower or Lewis type acidity that favors the formation of C1–C4 alkanes, aromatics and thiophene.

In a previous study we found that CH_3SH was significantly converted into H_2S and hydrocarbons only at high temperature [3,4]. For example, the highest conversions were obtained at 823 K: 77% on H-FER, 84% on H-Y and 99% on H-ZSM-5(15). Because one objective of this study is to decompose simultaneously C_2H_5SH and CH_3SH , experiments with C_2H_5SH were carried out at 823 K. At this temperature C_2H_5SH was fully converted with all catalysts.

Table 4

Products distribution on H-molecular sieves at 823 K and 6 h tos.

Catalyst	Coke (mg/100 mg)	Selectivity to S-products ^a (%)		Selectivity to C-products ^a (%)			C balance (%)
		H ₂ S	Sres ^b	C ₂ H ₄	C1–C4	BTX	
H-ferrierite	2.10	98.1	1.9	97.2	2.60	0.20	102.9
H-SAPO-34	0.90	93.8	6.2	91.1	8.50	0.40	99.5
H-Y	1.70	93.6	6.4	92.9	6.96	0.14	102.4
H-ZSM-5(15)	2.20	97.9	2.1	93.3	6.35	0.35	102.0
H-ZSM-5(40)	0.98	94.6	5.4	90.9	8.96	0.15	100.9
H-ZSM-5(75)	0.90	92.8	7.2	80.3	19.3	0.4	98.6
HZSM-5(15) 70 h ^c	2.40	97.2	2.8	94.5	5.10	0.4	99.0

^a The selectivity is defined as: (amount of product/amount of total products) × 100.^b Sres: CS₂ + thiophene.^c Averaged for a 70 h experiment.

The selectivities summarized in Table 4 are values averaged over the 6 h tos. A high selectivity to ethylene in C-containing products, from 80 to 97% was obtained. But, as discussed for a lower temperature (Table 2), the product distribution at 823 K also depends on the catalyst topology. The amount of coke formed after 6 h of reaction (determined by TG experiments, Fig. S4 in Supplementary information) was very low, i.e. 1–2 mg for 100 mg of catalyst. For all catalytic tests, the carbon balance, was very accurate, i.e. $101 \pm 1\%$. To gain a better insight into the catalyst deactivation, long-term experiments were carried out at 823 K in the presence of H-ZSM-5(15) sample. Full C₂H₅SH conversion maintains for 70 h tos with only small changes of selectivity (Fig. S5 in Supplementary information). Moreover, the coke amount (2.4 mg/100 mg_{cat}) is only slightly higher than that built up after 6 h of reaction, pointing out that the coke is generated mainly at the early stage of the process. This quantity of coke is much lower than that observed in the conversion of CH₃SH under comparable conditions [4]. Thus, when CH₃SH was processed in a dry feed (CH₃SH/N₂ = 0.5/99.5), the selectivity to coke amounted to 7.7%, but upon addition of 2% of water in the feed, the selectivity to coke decreased to 2.6%, at the cost of a small decrease of conversion from 95 to 93.5% [4]. The effect of water addition in the feed was also very beneficial to decrease the building up of coke in the C₂H₅SH conversion. Thus, in a 6 h tos experiment, at 823 K, with 2% of H₂O in the feed, only 0.53 mg/100 mg_{cat} was formed (Fig. S4 in Supplementary information). Additionally, the selectivities to ethylene and hydrocarbons do not change significantly by adding water in reaction.

3.2. Catalytic conversion of methyl/ethyl mercaptan mixture

Because H-ZSM-5(15) was the best catalyst for the conversion of C₂H₅SH (this study) and CH₃SH [4], we chose this zeolite to study the conversion of C₂H₅SH/CH₃SH mixtures. The catalytic decomposition of C₂H₅SH + CH₃SH was carried out at $\tau = 0.20$ g s mL⁻¹ (WHSV = 0.32 h⁻¹) and $\tau = 0.12$ g s mL⁻¹ (WHSV = 0.50 h⁻¹) at 823 K with a feed CH₃SH/C₂H₅SH/N₂ = 0.5/0.225/99.275. The complete conversion of both reactants was achieved only at $\tau = 0.20$ g s mL⁻¹ (WHSV = 0.32 h⁻¹). Under those conditions, the complete conversion of both mercaptans is maintained for 11 h tos before declining smoothly, with the appearance of dimethyl sulfide (Fig. 5). The carbon-containing products appearing in the gas phase are C₂H₄, CH₄, C1–C4 alkanes, BTX, CS₂, thiophene and only traces of unidentified sulphur-containing products. Nevertheless, the content of CS₂ starts rapidly increasing after 5 h of reaction.

Considering the wide variation of natural gas composition, a test with a higher ethylmercaptan concentration was performed with a mixture CH₃SH/C₂H₅SH/N₂ = 0.25/0.4/99.35. At 823 K and $\tau = 0.20$ g s mL⁻¹, for 13 h tos the catalyst exhibited a very good stability against deactivation (Fig. S6 in Supplementary information). Additionally, the concentration of CS₂

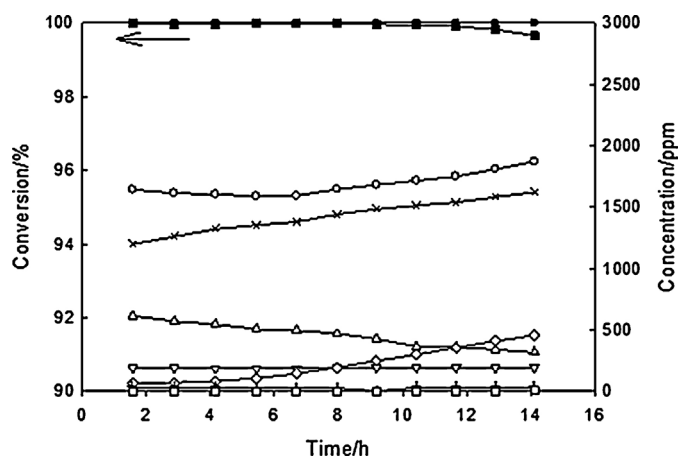


Fig. 5. Thiols decomposition on H-ZSM-5(15); (●) C₂H₅SH conversion, (■) CH₃SH conversion; concentrations: (□) dimethylsulfide, (○) C₂H₄, (×) CH₄, (Δ) BTEX, (▽) C1–C4, (◇) thiophene + CS₂, (+) S residual: feed: CH₃SH/C₂H₅SH/N₂ = 0.5/0.225/99.275 without water.

was less than 80 ppm and remains constant all test long, on the contrary of what observed in previous tests with a higher methylmercaptan concentration. Also, the amount of coke is significantly reduced, as shown by the TG experiments carried out on the spent catalysts (Fig. S7 supplementary information). In fact, it diminished from 7.7 mg/100 mg_{cat} with the mixture CH₃SH/C₂H₅SH/N₂ = 0.5/0.25/99.25 to 4.5 mg/100 mg_{cat} with CH₃SH/C₂H₅SH/N₂ = 0.25/0.4/99.35.

In a further experiment, we added 2% of water to the feed consisting of CH₃SH/C₂H₅SH/N₂ = 0.5/0.225/99.275. As shown in Fig. 6, the conversion of CH₃SH decreases only from 100% to 97% during 13 h tos. Additionally, the selectivity to CS₂ and coke significantly decreased. Indeed, the amount of coke formed on catalyst (determined by TG measurements, Fig. S8 Supplementary information) decreased from 7.7 mg/100 mg_{cat} in the absence of water to 4 mg/100 mg_{cat} in the presence of water.

Finally, the efficiency of a regeneration process was evaluated on the spent H-ZSM-5(15) after 13 h experiment in absence of water. It consists of an air calcination from 523 to 823 K by 50-K, 30-min steps, followed by a final step of 25 K up to 848 K lasting 1 h. The regenerated catalyst exhibits catalytic properties that are very similar to the fresh one (Fig. S9 vs. Fig. 5).

The results obtained in this last section clearly show that H-ZSM-5 zeolite is an effective catalyst for the selective conversion of the mixture ethyl–methyl–mercaptans into hydrocarbons (ethylene and methane) and H₂S. Also, we can conclude that CH₃SH is the main responsible for the deactivation of the catalyst.

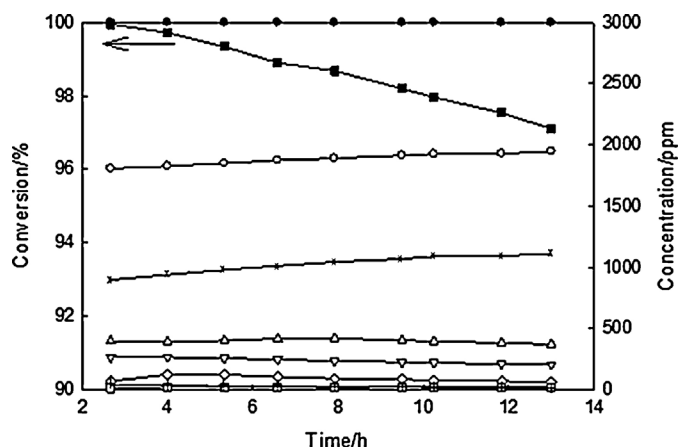


Fig. 6. Thiols decomposition on H-ZSM-5(15); (●) C_2H_5SH conversion, (■) CH_3SH conversion; concentrations: (□) dimethylsulfide, (○) C_2H_4 , (×) CH_4 , (Δ) BTX, (▽) C1–C4, (◇) thiophene+ CS_2 , (+) S residual; feed: $CH_3SH/C_2H_5SH/N_2 = 0.5/0.225/99.275$ with water.

4. Conclusion

Experimental results confirm that the conversion of C_2H_5SH into H_2S and ethylene can be successfully achieved in the presence of protonic molecular sieves. The kinetic parameters indicate that both the acid properties and solid topology play a crucial role in the mercaptan conversion. Zeolite H-ZSM-5 (Si/Al = 15), with MFI topology and high density of the acid site showed the highest activity and selectivity. Only small amount of coke is formed with that catalyst and thus it is stable for more than 70 h of TOS. CH_3SH in the methyl/ethyl mercaptan mixture is selectively transformed into methane and H_2S , but significant amounts of coke and aromatics are formed. When 2% of water was added in the gas feed the selectivity to coke drastically decreased.

Finally, we consider that the notable results reported in this study could be useful for developing a viable process for removing the mercaptans from natural gas. Thus, the selective catalytic

conversion of mercaptans into H_2S and hydrocarbons over acid solid catalysts could be incorporated as a stage into an integrated system, including the adsorption/desorption of sulfur compounds on molecular sieves, mercaptan conversion over zeolites and H_2S removal by absorption in basic solution. In a real process, the gas used for stripping the pre-adsorption bed will preferably be methane. This is a realistic solution, because, as we previously reported [4], similar results can be obtained in the mercaptan decomposition over zeolites using CH_3SH/N_2 or CH_3SH/CH_4 mixtures.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.03.026>.

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